



# PATENT SPECIFICATION

772,691

Date of Application and filing Complete Specification March 16, 1955

No. 7662/55.

Application made in Netherlands on March 19, 1954.

Complete Specification Published April 17, 1957.

Index at acceptance : Classes 1(2), E2A2; 32, C; and 37, K(2C: 3).

International Classification : —B01d. C01b. H01l.

## COMPLETE SPECIFICATION

### Improvements in or relating to the Manufacture of Silicon Carbide Crystals

We, PHILIPS ELECTRICAL INDUSTRIES LIMITED, of Spencer House, South Place, Finsbury, London, E.C.2, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to the production of silicon carbide crystals by sublimation and to semi-conductive devices comprising such crystals.

The production of well-formed large crystals by means of sublimation generally requires that the vapour pressure of the substance required to be sublimated is maintained low, that the temperature gradient in the vessel in which the sublimation is carried out is small and that the occurrence of gas currents is avoided as far as possible.

Due to the fact that silicon carbide produces a sufficient vapour pressure only at temperatures exceeding 2000° C. and that at such high temperatures of the usual heat resistance materials only carbon does not react with silicon carbide so as to cause the absorption of foreign impurities, the sublimation cannot be carried out in a closed gastight vessel. Consequently, the sublimation will have to be carried out at a total gas pressure equal to that in the furnace. The furnace itself can be closed so as to be gastight so that the sublimation can be carried out at any desired gas pressure.

When silicon carbide evaporates it dissociates into gaseous silicon and solid carbon. The silicon pressure is approximately 10 to 20% of the silicon carbide pressure. When a graphite vessel is used, silicon carbide vapour and also silicon vapour will diffuse through the wall into the furnace space on heating. Consequently well-formed crystals having

reasonably large dimensions and of satisfactory composition cannot be obtained in this manner with any degree of certainty.

The object of the invention is to provide an improved process for producing silicon carbide crystals.

According to the invention a process for producing silicon carbide crystals by means of sublimation is characterized in that the sublimation is carried out in an atmosphere of protective gas in a chamber the wall of which is of silicon carbide. A "protective gas" is defined to mean a gas which does not influence the composition of the silicon carbide at the temperature used in the process.

Silicon carbide is a very hard substance which cannot readily be machined so that a vessel entirely consisting of silicon carbide can be manufactured only with difficulty. However, the sublimation may be carried out in a graphite vessel lined with lumps of silicon carbide to provide said chamber. This lining may, for example, be provided by arranging a core in a graphite cylinder open at one end and filling the space between the graphite wall and the core with lumps of silicon carbide. After ramming the core can be removed carefully and the open upper end of the cylinder can be closed with a lump of silicon carbide. As an alternative, a graphite vessel may be lined with powdered silicon carbide to which water glass has been added as a binding agent.

If sublimation is required to be carried out at approximately atmospheric pressure, the sublimation vessel is heated to approximately 2500° C. By the use of suitable heat insulation, local temperature differences may be small, so that even at the points exhibiting the lowest temperatures in a reasonably short period of time, for example from 4 to 7 hours, at the low vapour pressure

[Price 3s. 6d.]

obtaining which is, for example, about 5 mms. to 50 mms. of mercury, which pressure is produced by the silicon carbide bounding the walls of the sublimation space, crystals having a major dimension of, for example, from 4 mms. to 10 mms. grow.

Due to the fact that in carrying out the process in accordance with the invention use is made of a chamber the wall of which is of silicon carbide, the equilibrium vapour pressure of silicon carbide and silicon will always obtain in this space so that the crystals which settle contain substantially no free carbon. It is true that material of the outer layer of the silicon carbide bounding the sublimation space will evaporate and dissociate and reach the furnace space but this substantially does not influence the sublimation.

The strength of gas currents in the sublimation chamber can be counteracted by causing the protective gas to flow through this chamber at a very low rate. Preferably, however, use is made of a vessel and sublimation chamber in which the chamber communicates with a gas source at one end only so that gas currents are further lessened.

Suitable gases for the protective gas atmosphere are inert rare gases, hydrogen and carbon monoxide. Hydrocarbons will decompose at the prevailing temperature to form  $C_2H_2 + H_2$  with the separation of carbon and hence hydrocarbons are preferably not used.

When pure starting material (impurities less than 0.002% by weight) is utilised, crystals substantially as clear as glass and having a resistivity of  $10^3 \Omega \text{cm}$  or higher can be obtained by a single sublimation. A starting material of sufficient purity can be produced in known manner by heating silicic acid and carbon to a temperature of approximately  $1800^\circ \text{C}$ . according to the reaction equation  $\text{SiO}_2 + 3 \text{C} \rightarrow \text{SiC} + 2 \text{CO}$ .

The sublimation produces a material purification of the silicon carbide. It is true that impurities present in the silicon carbide such as, for example, N, P, As, B, Al and Fe will also evaporate so that on condensation a certain amount of these impurities, which amount is dependent upon the partial pressure of the individual impurity vapours in the gas atmosphere, will be incorporated in the crystals. However the amount of impurity is low since the distribution coefficient (that is to say the ratio of the concentration of the impurity in the solid substance to that in the vapour) is small, for example approximately  $10^{-3}$  for

aluminium, independent of the partial pressure, and approximately  $10^{-3}$  for nitrogen, with a concentration of 0.5 mol.% in the protective gas at atmospheric pressure.

The presence of impurities in the crystals produces electrical conductivity, namely *n*-conductivity with elements having a valency exceeding 4, such as for example N, P, As, which act as donors, and *p*-conductivity with elements of a valency less than 4, for example B and, Al, which act as acceptors. When donor impurities are present the colour of the silicon carbide becomes green to green-black and when acceptor impurities are present it becomes blue to blue-black.

The amount of the donor and acceptor impurities can be controlled by means of the vapour pressure of the donor or acceptor in elementary form or in the form of a compound in the gas in which the sublimation is carried out. During sublimation, the partial pressure of the impurities in the sublimation space can be maintained constant. Consequently, in this event crystals are obtained having a composition which is substantially constant throughout.

Nitrogen may be used as a donor simply by adding nitrogen gas to the protective atmosphere. Phosphorus can be introduced in the gas in the form of  $\text{PCl}_3$  or  $\text{PH}_3$  and arsenic and antimony in the form of  $\text{AsCl}_3$  and  $\text{SbCl}_3$ , respectively.

The amount of aluminium required to produce crystals having *p*-conductivity can be controlled by adding it in the form of  $\text{AlCl}_3$ . However, in this event allowance should be made for the fact that in hydrogen at a temperature exceeding  $1000^\circ \text{C}$ . the reaction  $4 \text{AlCl}_3 + 6 \text{H}_2 + 3 \text{C} \rightarrow \text{Al}_4\text{C}_3 + 12 \text{HCl}$  proceeds and  $\text{Al}_4\text{C}_3$  at a temperature below  $2000^\circ \text{C}$ . does not have a sufficient vapour pressure. Consequently in the presence of  $\text{AlCl}_3$ , which up to  $3000^\circ \text{C}$ . itself does not react with C., the sublimation can be carried out only in an atmosphere of inert rare gas or carbon monoxide. A similar complication occurs if boron is added in the form of  $\text{BCl}_3$  and consequently in this event also sublimation is carried out in an inert rare gas or in carbon monoxide.

With a sufficient concentration of the impurities in the initial material it is also possible to produce *n*-type and *p*-type crystals. The addition of controlled amounts of the donor and acceptor impurities can be effected in the starting silicon carbide material. In order to produce this material use may, for example, be made of a mixture

of  $\text{SiO}_2 + \text{C}$  to which  $\text{Na}_3\text{PO}_4$  or  $\text{Al}_2\text{O}_3$  is added. The donor or acceptor is then previously built in the SiC lattice. However, a mixture of SiC and the impurity in elementary form or in the form of a compound may also be used as initial material. In accordance with the distribution coefficient during sublimation the separated crystals will have the desirable donor or acceptor concentration.

Crystals can be produced having adjacent zones of different conductivity, more particularly of opposite conductivity type, by adding locally a controlled amount of the donor and/or acceptor impurities to the crystals.

This can be effected by varying the vapour pressure of an impurity during sublimation and, if the formation of crystals having zones of opposite conductivity type is required, by causing the vapour pressure of donor and acceptor impurities respectively to predominate alternately.

As an alternative, the impurities can be added partly to the initial material and partly to the gas atmosphere. In order to produce crystals comprising  $p-n$  junctions use may, for example, be made of SiC containing a controlled amount of impurity as initial material which is sublimated in a protective gas together with an impurity which gives rise to the formation of silicon carbide having the opposite conductivity type. If in this case use is made of a protective gas containing a proportion of the last-mentioned impurity, which proportion may, if required, be varied periodically, silicon carbide will separate out which has a conductivity corresponding to the first-mentioned or last-mentioned impurity, respectively, according as the vapour pressure of the impurity originating from the initial material or the impurity which is added to the gas predominates in the sublimation atmosphere with the result that crystals having  $p-n$  junctions are obtained.

The silicon carbide crystals produced in accordance with the invention can be used in semi-conductive devices, such as rectifiers, transistors and voltage-dependent resistors.

The process according to the invention can be carried out with the use of an apparatus of the kind shown diagrammatically in the accompanying drawing. The figure shows a hollow graphite cylinder 1 open at one end and closed at the other. On the bottom and along the walls lumps of silicon carbide 2 are piled and the silicon carbide chamber is completed by a lump 3 of the same substance to provide a sublimation space 23. This

vessel 1 is arranged on a cylindrical member 4, which is filled with soot 5 to provide heat insulation and comprises small apertures 6. A slightly larger graphite cylinder 7 surrounds the vessel 1 and comprises an aperture 8 in its bottom 9. The upper end of the cylinder 7 is closed by a graphite member 10 in which a cylindrical member 11 made of graphite is arranged which similarly to the member 4 is filled with soot 12. The cylinder 7 also contains a number of transverse gratings 13. Below the bottom 9 an insulating member 15 is provided which is made of graphite and filled with soot 14 and comprises a duct 16. The whole is provided in a carbon furnace wall 17 which consists of a graphite cylinder open at both ends and having two sawcuts formed in it for a large part of its length which extends so as to be parallel to its longitudinal axis. At the sawed end of the cylinder, copper electrodes 18 comprising water cooling ducts 19 are arranged below each part between the sawcuts. An outer insulating jacket 20 and a filling of soot 21 are provided.

At the lower end of the apparatus, the protective gas used in sublimation can be introduced. This gas flows slowly through a supply pipe 22, the duct 16 and the apertures 8 and 6 and through apertures in and at the sides of the lump of silicon carbide 3 to the sublimation space 23 without giving rise therein to substantial gas currents.

Thereupon the gas passes through the apertures in the gratings 13, which are provided in the gas flow path in order to condense vapour carried along by the gas, and leaves the furnace through apertures 24.

A separate gas flow for protecting the carbon furnace wall 17 is introduced separately into the space between the graphite cylinder 7 and the insulating jacket 20.

Examples of the process according to the invention will now be given.

#### EXAMPLE I

A cylindrical graphite vessel which is open at one end, has an inner diameter of 70 mm and an outer diameter of 80 mm and is 130 mm long, is lined internally by piling lumps of pure silicon carbide (impurities less than 0.002% by weight) so as to surround a central mandrel 25 mm thick. Consequently the silicon carbide layer is approximately 20 to 25 mm thick. A layer of approximately equal thickness is arranged on the bottom of the vessel also and the open upper end of the vessel is closed by a lump of silicon carbide. The total amount of sili-

con carbide is approximately 500 gms.

The vessel is arranged in a furnace in the manner shown in the drawing and the furnace is well-evacuated under a bell.

5 Thereupon, pure hydrogen or argon is introduced until atmospheric pressure is attained and this gas is passed through at a rate of approximately 1 litre per minute measured at room temperature; this gas is  
10 also passed through the space between the cylinder 7 and the jacket 20. Thereupon the temperature in the furnace is raised in 1 hour to 2500° C.  $\pm 30^\circ$  C. and is maintained at this temperature for about  
15 6 hours. Finally, it is allowed to cool in approximately 5 hours.

The loosely piled silicon carbide has become a coherent unit which proves to be substantially entirely recrystallised. On  
20 the inner wall of the sublimation chamber very pure crystals are arranged.

Separated crystals are obtained by carefully breaking up the silicon carbide mass. The yield of useful crystals is from  
25 30 to 200. The remainder of the carbide mass can be used again.

The transparent and substantially colourless crystals obtained exhibit a very

slight *n*-conductivity, due to the presence of traces of nitrogen (less than  $10^{-4}$  mol.%) in the flowing gas, and have a resistivity of approximately 1000  $\Omega$ cm.

#### EXAMPLE II

By treating silicon carbide in the  
35 manner described in Example I in a gas flow to which nitrogen has been added and products of high *n*-conductivity are obtained. In the following table the resistivity, the analytically determined  
40 nitrogen content, the number of incorporated nitrogen atoms per cc. calculated therefrom and the number of current carriers per cc. determined from the Hall coefficient at a temperature of  
45 from 600° C. to 800° C. are listed for a number of crystals obtained in gas atmospheres of varying nitrogen content. The agreement between the electrically  
50 determined number of current carriers and the number of analytically determined nitrogen atoms is striking. For the sake of completeness it should be noted that the crystals were analysed by heating them to 2300° C. *in vacuo*, collecting  
55 the liberated gas and determining the nitrogen content thereof.

No.	Mol % of N <sub>2</sub> in H <sub>2</sub> at 1 atm.	Resistivity in $\Omega$ cm	Analytically determined % by weight of N <sub>2</sub> in crystal	Calculated from analysis atoms N/cc	Calculated from Hall coefficient electrons/cc
60					
	1 0.5	0.17	$1.2 \times 10^{-2}$	$1.65 \times 10^{18}$	$1.9 \times 10^{18}$
	2 2		$3.8 \times 10^{-2}$	$5.2 \times 10^{18}$	$5.6 \times 10^{18}$
65	3 13		$1.3 \times 10^{-2}$	$1.8 \times 10^{19}$	$4.1 \times 10^{19}$
	4 75	0.006	$4 \times 10^{-2}$	$5.8 \times 10^{19}$	$7.7 \times 10^{19}$

#### EXAMPLE III

Addition of Al permits silicon carbide crystals of *p*-conductivity to be produced. An apparatus of the kind shown  
70 in the drawing is filled with pure silicon carbide 2, 3 in the manner described in Example I. After evacuation under a bell pure argon is introduced until atmospheric pressure is attained and is there-  
75 after passed through at a rate of one litre per minute measured at room temperature. Argon is also passed between the cylinder 7 and the jacket 20. Thereafter, the furnace is heated and, when a temperature of from 1000° C. to 1500° C. is  
80 reached, AlCl<sub>3</sub> is added to the argon flow. The gas supply pipe 22 is maintained at a temperature of from 150° C. to  
85 200° C.

The AlCl<sub>3</sub> is added to the gas flow by passing the argon loaded with a chlorine-carbon compound, for example, CCl<sub>4</sub>, over aluminium at a temperature of from

400° C. to 500° C. The amount of CCl<sub>4</sub> 90 present in the gas is thus quantitatively converted into AlCl<sub>3</sub>. The CCl<sub>4</sub> concentration in the gas can be readily controlled by means of the temperature of the liquid CCl<sub>4</sub> and of the rate of flow of  
95 the argon which is passed through this liquid.

The AlCl<sub>3</sub> carried along by the gas flow reaches the sublimation space by diffusion.

The sublimation is carried out at a temperature of approximately 2500° C. for about 6 hours after which cooling is effected for approximately 5 hours. When the temperature in the sublimation space  
105 has dropped to approximately 2000° C., the atmosphere within the apparatus is changed to argon having no AlCl<sub>3</sub> added to it. In the following table the analytically determined aluminium content, the  
110 number of incorporated aluminium atoms per cc. calculated therefrom and the

number of current carriers per cc. at 500° C. to 600° C. determined from the Hall coefficient is given of a number of

crystals produced by sublimation in argon at atmospheric pressure with a varying AlCl<sub>3</sub> concentration.

No.	Mol % of AlCl <sub>3</sub> in argon at 1 atm.	Analytically determined % by weight of Al in crystal	Calculated from analysis atoms of Al cc.	From Hall coefficient holes/cc
1	0.0093			
2	0.056	0.003	2.10 <sup>18</sup>	3.10 <sup>17</sup>
3	0.53	0.014	1.10 <sup>19</sup>	N10 <sup>19</sup>
4	1.9	0.20	1.4 × 10 <sup>19</sup>	

15

## EXAMPLE IV

Initial use is made of SiC containing 0.3% by weight of aluminium, obtained by heating a mixture of carbon, silicic acid and aluminium oxide to a temperature of 2000° C. in an atmosphere of hydrogen. The product is subjected to a treatment as described in Example I with the use of carbon monoxide as the protective gas, and *p*-conductivity crystals are obtained having an Al-content of 0.005% by weight.

## EXAMPLE V

Pure silicon carbide is subjected to a treatment exactly similar to that described in Example III, in an atmosphere of argon containing 0.06 mol.% AlCl<sub>3</sub>, crystals of *p*-conductivity are produced. After these crystals have grown for 4 hours argon is introduced in which the AlCl<sub>3</sub> addition is substituted by 1 mol.% addition of nitrogen, after which the crystals grow for three hours during which time nitrogen-containing SiC is deposited. The occurrence of rectification shows that a *p-n* junction is produced in the crystals, which junction is visible due to colour difference.

What we claim is:—

1. A process for producing silicon carbide crystals by means of sublimation, characterized in that the sublimation is carried out in an atmosphere of protective gas in a chamber the wall of which is of silicon carbide.

2. A process as claimed in Claim 1, characterized in that sublimation is carried out in a graphite vessel which is lined with silicon carbide to provide said chamber.

3. A process as claimed in Claim 2, characterized in that sublimation is carried out in a graphite vessel which is lined with lumps of silicon carbide.

4. A process as claimed in any of Claims 2 and 3, characterized in that sublimation is carried out at a temperature of approximately 2500° C. in a protective gas at substantially atmospheric pres-

sure, the occurrence of local temperature differences being restricted by heat insulation and protective gas currents in the sublimation space reduced by the use of a vessel which communicates at one end with a gas source which supplies the gas atmosphere in the sublimation space.

5. A process as claimed in any of Claims 1 to 4, characterized in that sublimation is carried out in an atmosphere of inert rare gas.

6. A process as claimed in any of Claims 1 to 4, characterized in that the sublimation is carried out in an atmosphere of hydrogen.

7. A process as claimed in any of Claims 1 to 4, characterized in that the sublimation is carried out in an atmosphere of carbon monoxide.

8. A process as claimed in any of Claims 1 to 7, for producing crystals having *n*-conductivity, characterized in that the required amount of donor impurity is controlled by means of the vapour pressure of this impurity in elementary form or as a compound in the sublimation atmosphere.

9. A process as claimed in any of Claims 1 to 7, for producing crystals having *p*-conductivity, characterized in that the required amount of acceptor impurity is controlled by means of the vapour pressure of a compound of the impurity in the sublimation atmosphere.

10. A process as claimed in any of Claims 1 to 7, for producing crystals having *n*-conductivity, characterized in that the required amount of donor impurity is added to the initial silicon carbide material.

11. A process as claimed in any of Claims 1 to 7, for producing crystals having *p*-conductivity, characterized in that the required amount of acceptor impurity is added to the initial silicon carbide material.

12. A process as claimed in any of Claims 1 to 7, for producing crystals having adjacent zones of different con-

- ductivity, more particularly of opposite conductivity type, characterized in that the required amounts of acceptor and/or donor impurities are locally added to the  
5 crystals by varying the impurity and/or adjusting the vapour pressure of the or these impurities in elementary form or as a compound or compounds.
13. A process as claimed in any of  
10 Claims 1 to 7, for producing crystals having adjacent zones of different conductivity, more particularly of opposite conductivity type, characterized in that some impurity is added to the initial silicon carbide material and the remainder to  
15 the sublimation atmosphere.
14. A process as claimed in Claim 1, substantially as herein described in Example I, II, III, IV or V.
15. A silicon carbide crystal when produced by the process claimed in any of the preceding claims. 20
16. A semi-conductive device, more particularly a transistor, comprising a silicon carbide crystal as claimed in  
25 Claim 15.

T. D. THREADGOLD,  
Chartered Patent Agent,  
Century House, Shaftesbury Avenue,  
London, W.C.2,  
Agent for the Applicants.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1957.  
Published at the Patent Office, 25, Southampton Buildings, London, W.C.2, from which  
copies may be obtained.

772,691

COMPLETE SPECIFICATION

1 SHEET

This drawing is a reproduction of  
the Original on a reduced scale.

